Fabrication and Characterisation of Solid-state Electrochemical Switches

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Abstract

Solid-state electrochemical switches, also known as Quantised Conductance Atomic Switches (QCAS), have been investigated using reversible conversion of silver to silver sulphide for the switching. Electron-beam lithography and a custom plasma-based sulphidation technique have been employed for device fabrication, and optical ellipsometry has been used to accurately characterise the sulphidation reaction. The sulphide layer that is formed saturates at a thickness of 10-12 nm, which is ideal for these devices. Prototype devices, fabricated using nichrome as the inert electrode, have an OFF/ON resistance ratio of 1000, with an on-state resistance of 90 Ω.

Keywords: nanofabrication, solid-state switches

1 Introduction

Electronic switches are used extensively as memory storage devices and circuit elements. The important characteristics of switches for electrical applications include small size, for high density, fast switching speeds and high reliability. As device sizes are minimized and capacities of storage devices increase the size of the switches that these devices are based on must also reduce. Currently, transistors such as Field Effect Transistors (FETs) are used as switches. The improved memory density of storage devices such as FETs has been provided through the reduction of fabrication sizes and dimensions; this reduction is limited by the resolution of lithography equipment. Since 2001, the International Roadmap for Semiconductors [1] has begun to challenge the ability of MOSFET devices to provide the desired improvements and a wide array of interesting and exotic alternatives have since been proposed. Prospective device structures such as the Quantised Conductance Atomic Switch (QCAS) may provide the key to Moore's Law continuing to hold.

This project builds on the work completed in 2005 at the University of Canterbury [2] that, in turn was based upon work published by Terabe et al. [3]. This work demonstrated an electrically controllable, atomic size, electrochemical switch constructed from a silver/silver sulphide/platinum structure, such as that shown in Fig. 1. The small size and simple construction of the switch suggested that it could provide an alternative or addition to transistor-based integrated circuitry. In addition to the switching mechanism Terabe et al. investigated the occurrence of a physical phenomena called quantised conductance, in which multiple stable voltage levels are achieved; thus the switch was called a QCAS. In previous work at the University of Canterbury [2] a novel sulphidation technique was devised and functional devices formed. This project adds to that work by further characterising the sulphidation process, improving the fabrication process and investigating metals other than platinum for the inert cross-bar.

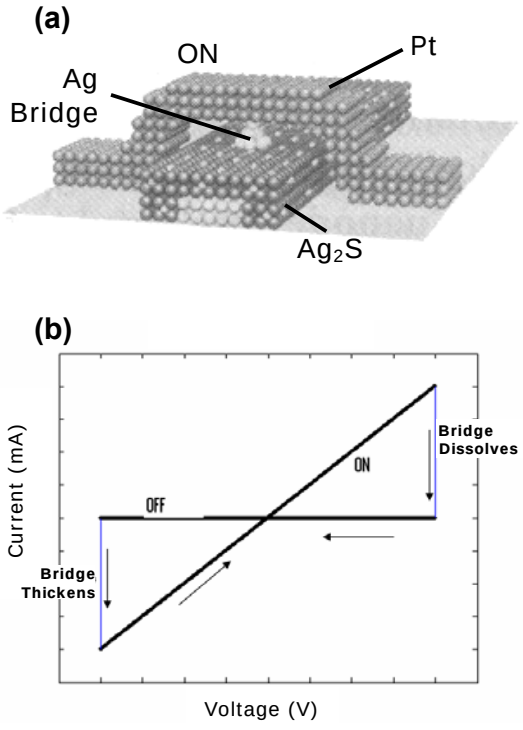

Figure 1: (a) Schematic of QCAS [3] (b) Empirical I-V characteristics of the QCAS

2 Review of QCAS Developments

Currently two major groups are publishing research on QCAS-related devices. A combined Japanese research team working at RIKEN and the National Institute Materials Science (NIMS) has published a series of articles and presentations on which the University of Canterbury devices were based. A second research group in Arizona has been studying the similar operations of an atomic switch based on a Ag/AgGeSe/Ni structure.

The Japanese Group first published related materials in 2001 [4]; this looked at the growth of silver through a silver sulphide. Over the following five years a number of developments were made [5-7], demonstrating the characteristics and ability for these structures to be fabricated on silicon. The current research position is best represented by [6] in which the QCAS (NanoBridge) is implemented as a copper/copper sulphide/(Ti/Pt/Al) structure. A number of applications of the QCAS are considered, including as reconfigurable large-scale integration (LSI) components, configurable logic cells and non-volatile memory. Outstanding issues include variation in threshold voltages, the requirement to have each QCAS accompanied by a transistor, and expensive top electrodes. The latter two issues are addressed in the research described here.

The Arizona research group has published papers [8-10] showing an atomic switch with a similar structure to the QCAS but using a Ag/AgGeSe/Ni chemical structure. The fabrication of this device is significantly different as silver is photodissolved into a thin film of germanium chalcogenide, however the operation process of bridge growth is thought to be similar. To date, the published material contains only data for single switches however different device dimensions have been demonstrated and characterised. The small size and large resistive change are of a level similar to that of the Japanese work. Based on the work of Kozicki et al., a group from Daejeon, Korea [11] has developed a similar device using Ag/AgGeTe/Ti structure.

There is further research into important features of the QCAS or related device being carried out. In Germany [12] silver and gold electrodes are used instead of platinum. A further Japanese article [13] uses Anodized Aluminium Oxide (AAO) tubes to avoid the need for electron beam lithography (EBL) equipment. The appearance of quantised conductance was discussed in the Nature article [3] and further work [14] has investigated the presence of this phenomenon in QCAS devices.

In 2004 research into the QCAS began at the University of Canterbury [2]. This work looked at replicating the Japanese QCAS device ($Ag/Ag_2S/Pt$) device using the equipment available at Canterbury. A novel sulphidation technique was developed and functioning QCAS devices were produced and demonstrated. Fabrication problems meant that the device was larger than desired and the production process was difficult. In particular the high-temperature required to deposit the platinum top electrode caused considerable problems (resist cracking and melting), as well as being expensive.

3 Theory of Operation

The formation and dissolution of the silver bridge in the QCAS device is thought to proceed through an ionic reaction of the silver and silver sulphide similar to the copper reactions detailed in Ref. [7]. From demonstrations of conductance in ionic/electronic reactions it has been supposed [5] that the bridge growth is due to an electrochemical reaction. A negative voltage to the top electrode provides a stream of electrons to the silver sulphide, causing the reaction

$$Ag^+ + e^- \rightarrow Ag \qquad (1)$$

This results in a bridge of silver growing through the sulphide until the other electrode is met. Similarly if a positive voltage is applied to the top electrode a stream of electrons is drawn from the silver layer, causing the opposite reaction to occur,

$$Ag \rightarrow Ag^+ + e^- . \qquad (2)$$

Thus a positive voltage being applied to the top electrode will cause the silver bridge to break down and the insulating layer to reform. The speed at which the QCAS switches is limited by the time taken for the silver bridges to form or dissolve through the sulphur layer. Terabe et al [3] achieved 1 MHz switching and argued that this limitation was due to measurement equipment and that the QCAS could switch in the low GHz; this has yet to be shown.

4 Device Fabrication

The QCAS fabrication process involved a series of procedures as outlined in Fig. 2 and further detailed by Thompson [2]. This began with the dicing of a p-type silicon nitride (SiN) wafer into one-centimetre square samples. Each sample then had a set of contact pads patterned to allow contact to be made to each QCAS device. Silver wires were routed between two contact pads and sulphidised before the top contact metal wires were placed across the silver wires. During this project a particular effort was made to ensure each of the processes stages could be fabricated cleanly and correctly to enable repeated production of QCAS.

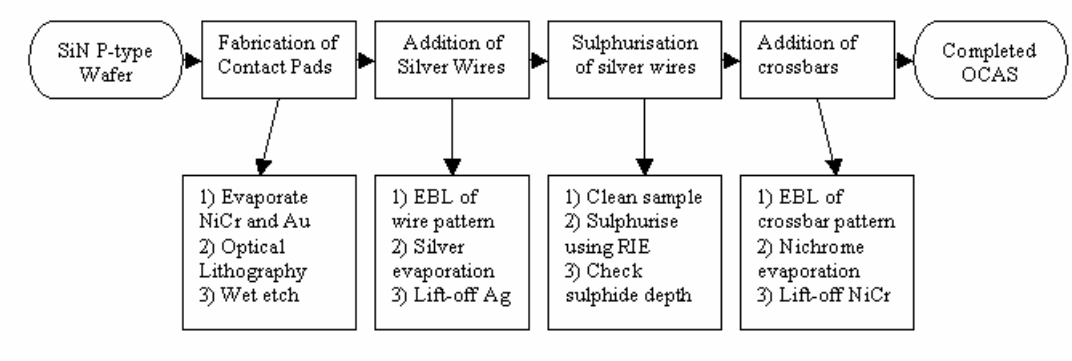

Figure 2: Fabrication stages for the UC QCAS devices

4.1 Contact Pads

The Nichrome (NiCr) under Gold (Au) contact pads were etched onto prepared 1 cm^2 silicon samples using an optical mask and chemical etch (Fig. 3). This required the evaporation of the two metals on to the wafer to the required thickness as well as using dilute acid to remove each of the metals. The major variable of the etch process is the time taken for the metal layers to dissolve, this was found to be highly variant on the strength of the acid. As the acid used was shared in the laboratory its strength would vary and the time taken to dissolve the metals would also change, this resulted in some samples being damaged. This problem was reduced by checking the purity of the acid etches before it was used.

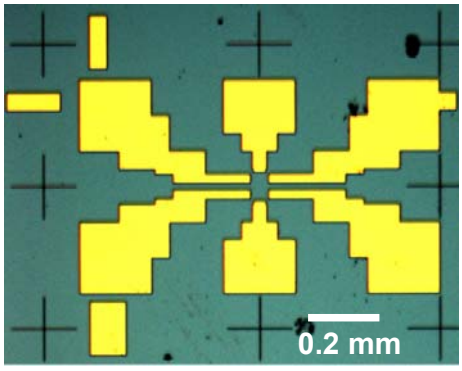

Figure 3: Example contact pad structure.

4.2 Silver Wire Patterning

The silver wires were fabricated using electron beam lithography (EBL) as they were sub-micron and could hence not be resolved using available optical lithography techniques. The mask was created using CAD software (L-Edit, Tanner Tools Inc.) based on measurements taken from the contact pads. Larger pads were patterned at the ends of the wires to ensure good conductivity to the contact pads. The pattern origin was set in the middle of the contact pads as this allowed the position to be calculated using the alignment markers on the wafer. As there were thirty separate contact pad patterns on each silicon sample the wire fabrication was repeated on each of the pads separately. This required using the EBL machine to accurately measure the distances between each pattern to allow the pattern array to be dimensioned.

Once a pattern had been written and developed, 100 nm of silver was thermally evaporated onto the sample. A lift-off process was then used to remove the unwanted silver by dissolving the remaining poly-methylmethacrylate (PMMA) electron-beam resist in acetone. Initially the silver wires would be destroyed in this process, leaving only the larger silver pads. This problem was prevented by increasing the dosage applied in the lithography process; this gives a longer EBL process but provides more consistent lift-off results.

4.3 Sulphidation

The sulphidation process used by the Japanese group could not be reproduced at Canterbury given the dangerous chemicals used and the equipment required. The sulphidation process developed by Thomson [2] used a Reactive Ion Etcher (RIE) and gaseous SF_6 to create a plasma containing sulphur ions that could then react with the silver wires. The procedure is operated at room temperature and at low power to avoid damaging the thin silver wires. The sulphidation process was first tested on a set of samples covered by 100 nm of silver. It was found that the process would not strike a plasma; further investigation revealed that a higher power etch was required to strike the initial plasma but after this the power could be reduced. It is theorized that this is because the initial etch leaves a residue after venting which is able to excite the next low power plasma.

Using these silver samples the nature of the sulphide formed was investigated in order to characterise the sulphidation process. The first technique used ellipsometry to measure the thickness of the sulphide layer of samples which had different length etches, and the results are shown in Fig. 4. The ellipsometer measures the change in angle as polarised light is

reflected off the sample and compares this with known data for the refractive indexes of the sample to estimate the thickness. The readings have large uncertainty margins as the refractive index of the silver can vary between samples. The resulting graph (Fig. 4) shows a reasonably clear saturation depth of between 10 nm and 12 nm. This saturation is not unexpected as many natural sulphide formations have saturation depths as the sulphur compounds are unable to penetrate through the sulphide layer.

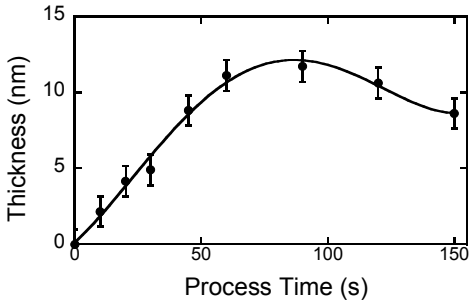

Figure 4: Silver sulphide thickness as a function of process time.

4.4 Crossbar Patterning

The QCAS fabrication process in 2005 [2] had difficulty in accurately creating the platinum top electrode. This was mainly due to the choice of platinum as the top electrode. Platinum (Pt) has a very high melting point and a low vapour pressure and hence requires a large electron beam current to evaporate at only a slow deposition rate; additionally platinum is a very expensive metal. In the QCAS fabrication this resulted in the PMMA cracking, causing additional platinum wires to form across the sample as shown in Fig. 5. In related QCAS research a number of different top electrode metals have been used; instead of continuing to work around platinum's problems a new metal was chosen.

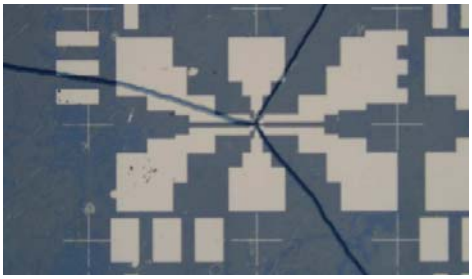

Figure 5: PMMA cracking due to high temperatures during metal deposition [2].

In choosing an appropriate metal to use for the top contact, the most important factor was choosing a metal that would allow function of the QCAS. The properties of platinum were investigated, in order to understand why it had been used in the Japanese research. Platinum is a non-reactive metal with high electrical conductivity; this means that it provides a very inert top conductor that will cause few side effects to QCAS operation. Platinum's inertness was important when quantised conductance states of QCAS devices were being examined since even small interactions may have distorted the experiments. However the available research showed devices made using copper, gold, and nickel creating functioning QCAS devices.

As the research literature suggested that the device could work with a range of metal top electrodes, nichrome (NiCr) was used. This selection was based on fabrication ease, expense, and availability. Nichrome is a low cost metal and is used widely in the microelectronics industry; hence the chemical properties are well known. NiCr evaporates at a much higher deposition rate than platinum and at lower temperatures. The NiCr also bonds well with silicon during evaporation, creating strong wires and avoiding the problems that arose with the silver lift-off. A limitation of NiCr is that it has a moderate to high resistivity that would increase the resistance of the QCAS in both on and off states.

An SEM image of a pair completed devices is shown in Fig. 6; these consist of two 500-nm wide sulphidised silver wires (running north-south in the image) overlaid by a single 2-µm wide NiCr crossbar. The two silver crossbars are very well defined and are well aligned with the contact pads. The NiCr crossbar is wider than desired but is very clean and continuous.

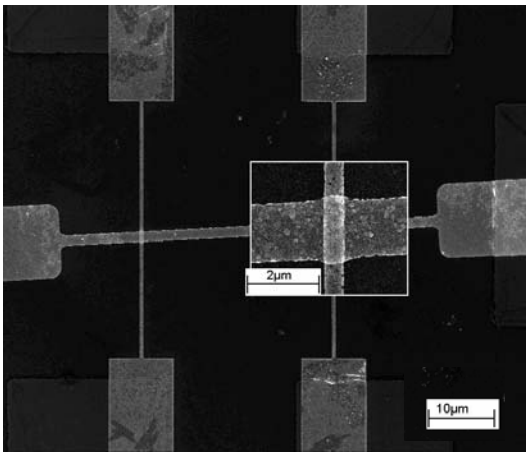

Figure 6: SEM micrograph of a pair of QCAS devices fabricated with a NiCr crossbar.

The improvements made to the fabrication processes can be seen through comparison to the devices published in previous research at the University of Canterbury [2], which are shown in Fig. 7. These devices functioned well, but the fabrication techniques introduced rougher wires, uneven surfaces and residual materials around the device. In particular, there is considerable disorder at the cross point, which potentially could affect device operation and yield.

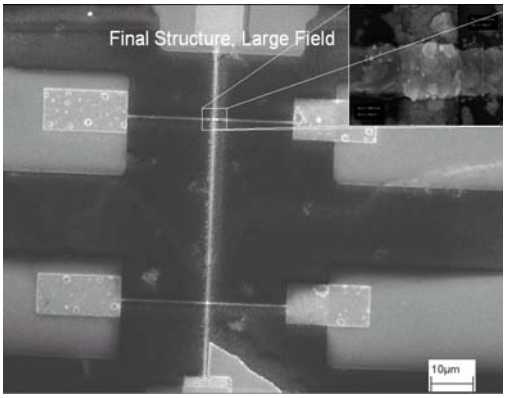

Figure 7: Previous UC QCAS devices with Pt crossbars [2], showing rough wire surfaces and additional material around the crossbar.

5 Device Testing

Device testing was carried out through the use of a parameter analyser to allow contact to be made to the individual QCAS devices or sections of the QCAS. The equipment set-up connected a probe to each end of the device under measurement and swept the voltage whilst measuring the current and calculating the resistance from the current voltage relationship. Measurements were taken for each section of the QCAS: the silver wires, the sulphidised silver wires and the NiCr cross wires as well as attempting measurements for the device switching. The results, listed in Table 1 show the approximate resistances of each of the QCAS sections. As expected, the sulphidation causes a small increase in the resistance of the silver wires and the NiCr cross wires have a larger resistance than the silver wires.

Table 1: Testing results for the sections of the QCAS

Device Section	Av. Resistance (Ω)
Silver wires	51
Sulphidised silver wires	58
Nichrome wires	141

As described above, the individual parts of the QCAS were found to have the expected resistance relationships. However when the complete QCAS was assembled conduction could not be achieved through either the silver sulphide wires or NiCr cross-wires. With further investigation it was found that the sulphidation process had damaged the silver wires and it is thought that the evaporation process caused further deterioration, creating breaks in the silver wires, as shown in Fig. 8. It is proposed that the breaks and general roughness of the silver caused the NiCr to fracture when it passed over it. The characterisation of the sulphidation process suggested that a shorter process time could create an equivalent sulphide depth and be less destructive.

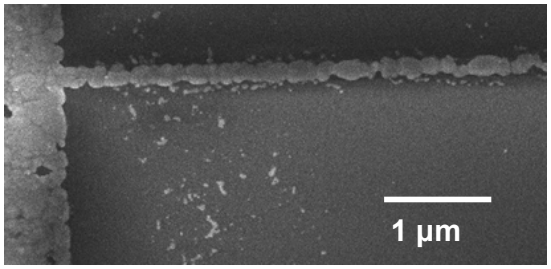

Figure 8: Breaks in the silver wires after sulphidation and crossbar deposition.

Another sample was constructed using a 45s sulphidation process, which according to Fig. 4 should also give approximately 10 nm of sulphide. SEM inspection of these devices (Fig. 6) show that the wires were far less damaged and had the number of devices conducting per sample increased substantially. The NiCr crossbars were overdeveloped on this sample and are hence wider than desired, however this should affect only the switching characteristics and not the switching itself. This device was tested and some basic switching was observed. A QCAS device demonstrated an initial off-state resistance of between 80 and 160 kΩ as shown in Fig. 9(a). Applying a 2 V signal to the NiCr electrode caused a switch to an on-state resistance of 90 Ω as shown in Fig. 9(b).

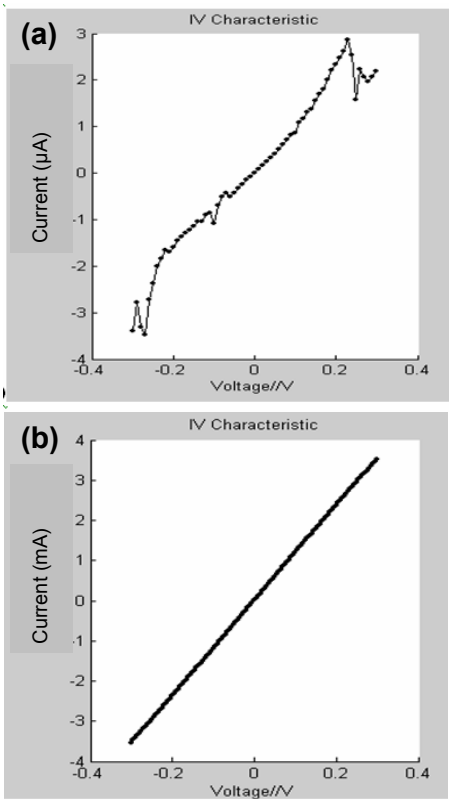

Figure 8: Current-voltage characteristic of a QCAS device (a) before and (b) after applying a 2 V switching signal to the device.

In comparison to Thomson's devices [2], the off/on ratio appears similar, at approximately 1000, but a lower on and off state resistance is present. The lower resistances are probably due to the larger wire widths used in these devices. A switch returning the QCAS to the off-state was attempted but not achieved, however the presence of a conducting device from which partial switching characteristic were obtained demonstrates the functioning of the adapted QCAS fabrication process. Further investigation of the device yield and consistency between devices on the same sample would enhance the QCAS research at the University of Canterbury.

6 Conclusions

This project has extended the research about the quantised conductance atomic switch at the University of Canterbury (UoC). In particular, the UoC fabrication process has been improved; and an alternative metal for use as the top electrode has been investigated.

The progress and improvement of the fabrication stages of the QCAS at Canterbury has been a successful part of this project. Each of the stages was repeated and special effort was made to characterise the sulphidation process. As a result, the final devices are much cleaner, have better defined components and less residue present. In addition, the characterisation of the process demonstrated a depth saturation of 10 to 12 nm of silver sulphide from 45 s onwards, meaning that considerably shorter process times can be used. Finally, the use of NiCr crossbars has been demonstrated, which overcomes the expense and problems previously faced with Pt crossbars. These major improvements in QCAS fabrication will enable high device yields and more consistent operation of working devices.

7 Acknowledgements

We gratefully acknowledge technical assistance from Helen Devereux, Gary Turner, and other members of the Department of Electrical and Computer Engineering at the University of Canterbury.

8 References

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